

## WEST Search History

DATE: Monday, September 27, 2004

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<i>DB=PGPB,USPT,USOC,EPAB,JPAB,DWPI,TDBD; PLUR=YES; OP=ADJ</i>			
<input type="checkbox"/>	L13	L12 and (carbonate or bicarbonate or sulfat\$ or phosphat\$)	5
		5051129.pn. or 5205860.pn. or 5527931.pn. or 6258454.pn. or	
<input type="checkbox"/>	L12	5562761.pn. or 3560385.pn. or 3730701.pn. or 3794736.pn. or 3814739.pn. or 3860709.pn. or 4282366.pn. or 4408996.pn. or 4504541.pn. or 4615937.pn. or 4692374.pn.	38
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<input type="checkbox"/>	L10	2637623	23
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<input type="checkbox"/>	L8	L2 and (carbonate or bicarbonate or sulfat\$ or phosphat\$) and (silane or silaxane)	51
<input type="checkbox"/>	L7	8/\$.ccls. and dianion	10
<input type="checkbox"/>	L6	L3 and dianion	0
<input type="checkbox"/>	L5	L3 and (carbonate or bicarbonate or sulfat\$ or phosphat\$) and (silane or silaxane)	2
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		8/632.cccls. or 8/ 636.cccls. or 8/490.cccls. or 8/133.cccls. or	
<input type="checkbox"/>	L2	8/115.51.cccls. or 8/115.54.cccls. or 8/115.55.cccls. or 8/115.64.cccls. or 8/115/68.cccls.	2342
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L3: Entry 1 of 11

File: USPT

Jan 6, 2004

DOCUMENT-IDENTIFIER: US 6673118 B2

TITLE: Method for refreshing, deodorizing and finishing garments

Detailed Description Text (9):

The presence of the highly preferred surfactant promotes spreading of the solution and the highly preferred antimicrobial active provides improved odor control as well as antimicrobial action, by minimizing the formation of odors. Both the surfactant and the antimicrobial active provide improved performance and the mixture is especially good. When the compositions are applied in the form of the very small particles (droplets), as disclosed hereinbefore, additional benefits are found, since the distribution is even further improved and overall performance is improved.

Detailed Description Text (40):

The surfactant, provides a low surface tension that permits the composition to spread readily and more uniformly on hydrophobic surfaces. It has been found that the aqueous solution, without such a surfactant will not spread satisfactorily. The spreading of the composition also allows it to dry faster, so that the treated material is ready to use sooner. Furthermore, the composition containing a surfactant can penetrate hydrophobic, oily soil better for improved malodor control. The composition containing a cyclodextrin-compatible surfactant also provides improved "in-wear" electrostatic control. For concentrated compositions, the surfactant facilitates the dispersion of many actives such as antimicrobial actives and perfumes in the concentrated aqueous compositions.

Detailed Description Text (64):

The preparation of polyalkylene oxide polysiloxanes is well known in the art. Polyalkylene oxide polysiloxanes of the present invention can be prepared according to the procedure set forth in U.S. Pat. No. 3,299,112, incorporated herein by reference. Typically, polyalkylene oxide polysiloxanes of the surfactant blend of the present invention are readily prepared by an addition reaction between a hydrosiloxane (i.e., a siloxane containing silicon-bonded hydrogen) and an alkenyl ether (e.g., a vinyl, allyl, or methallyl ether) of an alkoxy or hydroxy end-blocked polyalkylene oxide). The reaction conditions employed in addition reactions of this type are well known in the art and in general involve heating the reactants (e.g., at a temperature of from about 85.degree. C. to 110.degree. C.) in the presence of a platinum catalyst (e.g., chloroplatinic acid) and a solvent (e.g., toluene).

Detailed Description Text (66):

wherein R is an alkyl group. Examples of this type of surfactants are

available from the Dow Chemical Company under the trade name Dowfax.RTM. wherein R is a linear or branched C.<sub>sub.6</sub> -C.<sub>sub.16</sub> alkyl group. An example of these cyclodextrin-compatible anionic surfactant is Dowfax 3B2 with R being approximately a linear C.<sub>sub.10</sub> group. These anionic surfactants are preferably not used when the antimicrobial active or preservative, etc., is cationic to minimize the interaction with the cationic actives, since the effect of both surfactant and active are diminished.

Detailed Description Text (71):

Antimicrobial Active

Detailed Description Text (72):

The solubilized, water-soluble antimicrobial active, C., is useful in providing protection against organisms that become attached to the treated material. Preferably, the antimicrobial should be cyclodextrin-compatible, e.g., not substantially forming complexes with the cyclodextrin in the odor absorbing composition. The free, uncomplexed antimicrobial, e.g., antibacterial, active provides an optimum antibacterial performance.

Detailed Description Text (73):

Sanitization of ballistic fabrics can be achieved by the compositions of the present invention containing, antimicrobial materials, e.g., antibacterial halogenated compounds, quaternary compounds, and phenolic compounds.

Detailed Description Text (75):

Some of the more robust cyclodextrin-compatible antimicrobial halogenated compounds which can function as disinfectants/sanitizers as well as finish product preservatives (vide infra), and are useful in the compositions of the present invention include 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with hydrochloric, acetic and gluconic acids. The diacetate salt is highly water-soluble, about 70% in water, and the diacetate salt has a solubility of about 1.8% in water. When chlorhexidine is used as a sanitizer in the present invention it is typically present at a level of from about 0.001% to about 0.4%, preferably from about 0.002% to about 0.3%, and more preferably from about 0.05% to about 0.2%, by weight of the usage composition. In some cases, a level of from about 1% to about 2% may be needed for virucidal activity.

Detailed Description Text (76):

Other useful biguanide compounds include Cosmocil.RTM. CQ.RTM., Vantocil.RTM. IB, including poly (hexamethylene biguanide) hydrochloride. Other useful cationic antimicrobial agents include the bis-biguanide alkanes. Usable water soluble salts of the above are chlorides, bromides, sulfates, alkyl sulfonates such as methyl sulfonate and ethyl sulfonate, phenylsulfonates such as p-methylphenyl sulfonates, nitrates, acetates, gluconates, and the like.

Detailed Description Text (77):

Examples of suitable bis biguanide compounds are chlorhexidine; 1,6-bis-(2-ethylhexylbiguanidohexane)dihydrochloride; 1,6-di-(N.<sub>sub.1</sub>,N.<sub>sub.1</sub> '-phenyldiguanido-N.<sub>sub.5</sub>,N.<sub>sub.5</sub> ')-hexane tetrahydrochloride; 1,6-di-(N.<sub>sub.1</sub>,N.<sub>sub.1</sub> '-phenyl-N.<sub>sub.1</sub>,N.<sub>sub.1</sub> '-

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N.<sub>sub.5</sub>,N.<sub>sub.5</sub> ') -hexane tetrahydrochloride; and mixtures thereof; more preferably, 1,6-di(N.<sub>sub.1</sub>,N.<sub>sub.1</sub> '-o-chlorophenyldiguanido-N.<sub>sub.5</sub>,N.<sub>sub.5</sub> ') -hexane dihydrochloride; 1,6-di(N.<sub>sub.1</sub>,N.<sub>sub.1</sub> '-2,6-dichlorophenyldiguanido-N.<sub>sub.5</sub>,N.<sub>sub.5</sub> ') hexane dihydrochloride; 1,6-di(N.<sub>sub.1</sub>,N.<sub>sub.1</sub> '-2,4-dichlorophenyldiguanido-N.<sub>sub.5</sub>,N.<sub>sub.5</sub> ') hexane tetrahydrochloride; 1,6-di[N.<sub>sub.1</sub>,N.<sub>sub.1</sub> '-.alpha.- (p-chlorophenyl) ethyldiguanido-N.<sub>sub.5</sub>,N.<sub>sub.5</sub> '] hexane dihydrochloride; .omega.: .omega. 'di(N.<sub>sub.1</sub>,N.<sub>sub.1</sub> '-p-chlorophenyldiguanido-N.<sub>sub.5</sub>,N.<sub>sub.5</sub> ')m-xylene dihydrochloride; 1,12-di(N.<sub>sub.1</sub>,N.<sub>sub.1</sub> '-p-chlorophenyldiguanido-N.<sub>sub.5</sub>,N.<sub>sub.5</sub> ') dodecane dihydrochloride; 1,6-di(N.<sub>sub.1</sub>,N.<sub>sub.1</sub> '-o-chlorophenyldiguanido-N.<sub>sub.5</sub>,N.<sub>sub.5</sub> ') hexane dihydrochloride; 1,6-di(N.<sub>sub.1</sub>,N.<sub>sub.1</sub> '-p-chlorophenyldiguanido-N.<sub>sub.5</sub>,N.<sub>sub.5</sub> ') -hexane tetrahydrochloride; and mixtures thereof. As stated hereinbefore, the bis biguanide of choice is chlorhexidine its salts, e.g., digluconate, dihydrochloride, diacetate, and mixtures thereof.

Detailed Description Text (79):

A wide range of quaternary compounds can also be used as antimicrobial actives. Non-limiting examples of useful quaternary compounds include: (1) benzalkonium chlorides and/or substituted benzalkonium chlorides such as commercially available Barquat.RTM. (available from Lonza), Maquat.RTM. (available from Mason), Variquat.RTM. (available from Witco/Sherex), and Hyamine.RTM. (available from Lonza); (2) di(C.<sub>sub.6</sub> -C.<sub>sub.14</sub>)alkyl di short chain (C.<sub>sub.1</sub>-4 alkyl and/or hydroxyalkyl) quaternary such as Bardac.RTM. products of Lonza, (3) N-(3-chloroallyl) hexaminium chlorides such as Dowicide.RTM. and Dowicil.RTM. available from Dow; (4) benzethonium chloride such as Hyamine.RTM. 1622 from Rohm & Haas; (5) methylbenzethonium chloride represented by Hyamine.RTM. 10X supplied by Rohm & Haas, (6) cetylpyridinium chloride such as Cepacol chloride available from of Merrell Labs. Examples of the preferred dialkyl quaternary compounds are di(C.<sub>sub.8</sub> -C.<sub>sub.12</sub>)dialkyl dimethyl ammonium chloride, such as didecyldimethylammonium chloride (Bardac 22), and dioctyldimethylammonium chloride (Bardac 2050). Typical concentrations for biocidal effectiveness of these quaternary compounds range from about 0.001% to about 0.8%, preferably from about 0.005% to about 0.3%, more preferably from about 0.01% to about 0.2%, and even more preferably from about 0.03% to about 0.1%, by weight of the usage composition. The corresponding concentrations for the concentrated compositions are from about 0.003% to about 2%, preferably from about 0.006% to about 1.2%, and more preferably from about 0.1% to about 0.8% by weight of the concentrated compositions.

Detailed Description Text (80):

The surfactants, when added to the antimicrobials tend to provide improved antimicrobial action. This is especially true for the siloxane surfactants, and especially when the siloxane surfactants are combined with the chlorhexidine antimicrobial actives.

Detailed Description Text (88):

Non-limiting examples of the more preferred hydrophilic perfume ingredients are allyl amyl glycolate, allyl caproate, amyl acetate, amyl propionate, anisic aldehyde, anisyl acetate, anisole, benzaldehyde, benzyl acetate, benzyl acetone, benzyl alcohol, benzyl formate, benzyl iso valerate, benzyl propionate, beta gamma hexenol, calone, camphor gum, laevo-carveol, d-carvone, laevo-carvone, cinnamic alcohol, cinnamyl acetate, cinnamic alcohol, cinnamyl formate, cinnamyl

propionate, cis-jasmone, cis-3-hexenyl acetate, coumarin, cuminic alcohol, cuminic aldehyde, Cyclal C, cyclogalbanate, dihydroeuginol, dihydro isojasmonate, dimethyl benzyl carbinol, dimethyl benzyl carbonyl acetate, ethyl acetate, ethyl aceto acetate, ethyl amyl ketone, ethyl anthranilate, ethyl benzoate, ethyl butyrate, ethyl cinnamate, ethyl hexyl ketone, ethyl maltol, ethyl-2-methyl butyrate, ethyl methylphenyl glycidate, ethyl phenyl acetate, ethyl salicylate, ethyl vanillin, eucalyptol, eugenol, eugenyl acetate, eugenyl formate, eugenyl methyl ether, fenchyl alcohol, flor acetate (tricyclo decenyl acetate), fructose, frutene (tricyclo decenyl propionate), geraniol, geranyl oxyacetaldehyde, heliotropin, hexenol, hexenyl acetate, hexyl acetate, hexyl formate, hinokitiol, hydratropic alcohol, hydroxycitronellal, hydroxycitronellal diethyl acetal, hydroxycitronellol, indole, isoamyl alcohol, iso cyclo citral, isoeugenol, isoeugenyl acetate, isomenthone, isopulegyl acetate, isoquinoline, keone, ligustral, linalool, linalool oxide, linalyl formate, lyral, menthone, methyl acetophenone, methyl amyl ketone, methyl anthranilate, methyl benzoate, methyl benzyl acetate, methyl cinnamate, methyl dihydrojasmonate, methyl eugenol, methyl heptenone, methyl heptine carbonate, methyl heptyl ketone, methyl hexyl ketone, methyl isobutenyl tetrahydropyran, methyl-N-methyl anthranilate, methyl beta naphthyl ketone, methyl phenyl carbonyl acetate, methyl salicylate, nerol, nonalactone, octalactone, octyl alcohol (octanol-2), para-anisic aldehyde, para-cresol, para-cresyl methyl ether, para hydroxy phenyl butanone, para-methoxy acetophenone, para-methyl acetophenone, phenoxy ethanol, phenoxyethyl propionate, phenyl acetaldehyde, phenylacetaldehyde diethyl ether, phenylethyl oxyacetaldehyde, phenyl ethyl acetate, phenyl ethyl alcohol, phenyl ethyl dimethyl carbinol, prenol acetate, propyl butyrate, pulegone, rose oxide, safrole, terpineol, vanillin, viridine, and mixtures thereof.

Detailed Description Text (93):

There are also hydrophilic ingredients of group (a) that have a significantly low detection threshold, and are especially useful in the composition of the present invention. Examples of these ingredients are allyl amyl glycolate, anethole, benzyl acetone, calone, cinnamic alcohol, coumarin, cyclogalbanate, Cyclal C, cymal, 4-decenal, dihydro isojasmonate, ethyl anthranilate, ethyl-2-methyl butyrate, ethyl methylphenyl glycidate, ethyl vanillin, eugenol, flor acetate, florhydral, fructose, frutene, heliotropin, keone, indole, iso cyclo citral, isoeugenol, lyral, methyl heptine carbonate, linalool, methyl anthranilate, methyl dihydrojasmonate, methyl isobutenyl tetrahydropyran, methyl beta naphthyl ketone, beta naphthol methyl ether, nerol, para-anisic aldehyde, para hydroxy phenyl butanone, phenyl acetaldehyde, vanillin, and mixtures thereof. Use of low odor detection threshold perfume ingredients minimizes the level of organic material that is released into the atmosphere.

Detailed Description Text (100):

Chelators, e.g., ethylenediaminetetraacetic acid (EDTA), hydroxyethylene-diaminetriacetic acid, diethylenetriaminepentaacetic acid, and other aminocarboxylate chelators, and mixtures thereof, and their salts, and mixtures thereof, can optionally be used to increase antimicrobial and preservative effectiveness against Gram-negative bacteria, especially *Pseudomonas* species. Furthermore, aminocarboxylate chelators can help, e.g., maintaining product clarity, protecting

fragrance and perfume components, and preventing rancidity and off odors.

Detailed Description Text (101):

The optional chelators are present in the compositions of this invention at levels of, typically, from about 0.01% to about 0.3%, more preferably from about 0.02% to about 0.1%, most preferably from about 0.02% to about 0.05% by weight of the usage compositions to provide antimicrobial efficacy in this invention.

Detailed Description Text (103):

Metallic salts can be added to the compositions of the present invention for odor absorption and/or antimicrobial benefit. The metallic salts are selected from the group consisting of copper salts, zinc salts, and mixtures thereof.

Detailed Description Text (106):

In addition to the metallic salts described above, other salts such as alkali metal carbonate and/or alkali metal bicarbonate salts may also be included in the compositions of the present invention.

Detailed Description Text (113):

Solubilized, water-soluble, antimicrobial preservatives can be added to the compositions of the present invention.

Detailed Description Text (114):

Antimicrobial preservatives useful in the present invention include biocidal compounds, i.e., substances that kill microorganisms, or biostatic compounds, i.e., substances that inhibit and/or regulate the growth of microorganisms. List of suitable preservatives is found in U.S. Pat. No. 5,714,137.

Detailed Description Text (127):

The composition of the present invention can optionally contain adjunct odor-controlling materials, chelating agents, antistatic agents, insect and moth repelling agents, colorants, especially bluing agents, antioxidants, superspreaders, clarifiers, other silicone compounds and emulsions, viscosity control agents, anti-clogging agents, buffering agents, fabric care saccharides, polysaccharides, oligosaccharides, and mixtures thereof in addition to the cyclodextrin molecules. The total level of optional ingredients is low, preferably less than about 5%, more preferably less than about 3%, and even more preferably less than about 2%, by weight of the usage composition. These optional ingredients exclude the other ingredients specifically mentioned hereinbefore. Incorporating adjunct odor-controlling materials can enhance the capacity of the cyclodextrin to control odors as well as broaden the range of odor types and molecule sizes, which can be controlled. Such materials include, for example, metallic salts, water-soluble cationic and anionic polymers, zeolites, water-soluble bicarbonate salts, and mixtures thereof.

Detailed Description Text (130):

Organic salts useful in this invention include, magnesium, sodium, lithium, potassium, zinc, and aluminum salts of the carboxylic acids including formate, acetate, propionate, pelargonate, citrate, gluconate, lactate aromatic acids e.g. benzoates, phenolate and substituted benzoates or phenolates, such as phenolate, salicylate,

polyaromatic acids terephthalates, and polyacids e.g. oxylate, adipate, succinate, benzeneddicarboxylate, benzenetricarboxylate. Other useful organic salts include carbonate and/or hydrogencarbonate (HCO<sub>3</sub>.sub.3.sup.-1) when the pH is suitable, alkyl and aromatic sulfates and sulfonates e.g. sodium methyl sulfate, benzene sulfonates and derivatives such as xylene sulfonate, and amino acids when the pH is suitable. Electrolytes can comprise mixed salts of the above, salts neutralized with mixed cations such as potassium/sodium tartrate, partially neutralized salts such as sodium hydrogen tartrate or potassium hydrogen phthalate, and salts comprising one cation with mixed anions.

Detailed Description Text (143):

As used herein, the phrase "in association with" means the set of instructions are either directly printed on the container or substrate itself or presented in a separate manner including, but not limited to, a brochure, print advertisement, electronic advertisement, and/or broadcast communication, so as to communicate the set of instructions to a consumer of the article of manufacture. The set of instructions preferably comprises the instruction to apply an effective amount of the composition, preferably by spraying, to provide the indicated benefit, e.g., wrinkle reduction, and, optionally, antimicrobial action, and/or anti-static effect, etc. and, also optionally, the provision of odor control and/or reduction.

Current US Original Classification (1):  
8/115.51

Current US Cross Reference Classification (1):  
8/115.6

Current US Cross Reference Classification (2):  
8/147

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L8: Entry 19 of 51

File: USPT

Mar 16, 1999

DOCUMENT-IDENTIFIER: US 5883185 A

TITLE: Water soluble fiber-treating agent and method of making

Brief Summary Text (9):

We have found that a reaction product resulting from co-hydrolysis and condensation among (A) a fluorinated alkyl group-containing alkoxysilane of formula (1) and/or a partial hydrolyzate thereof, (B) an alkyl group-containing alkoxysilane of formula (2) and/or a partial hydrolyzate thereof, (C) an amino group-containing alkoxysilane of formula (3) and/or a partial hydrolyzate thereof, and (D) an epoxy group-containing alkoxysilane of formula (4) and/or a partial hydrolyzate thereof, the formulae being shown below, is useful as an active ingredient of a fiber treating agent. Since the fluorinated alkyl group-containing silane compound, which is effective as a water repellent component, itself is given water solubility, this reaction product is readily soluble in water and fully shelf stable, and imparts satisfactory and long lasting water repellency. Also since active hydrogen of an amino group is appropriately blocked with the epoxy group-containing silane compound, fibers treated with this reaction product undergo less yellowing on their surface. That is, there is obtained a water soluble fiber-treating agent which has overcome the problems of prior art fiber treating agents. We have also found that the above-mentioned reaction product is consistently prepared by effecting (partial) co-hydrolysis between components (A) and (B) to form a (partial) hydrolyzate, effecting condensation reaction of the (partial) hydrolyzate with component (C), and then effecting further condensation reaction with component (D) to thereby form a co-hydrolysis/condensation reaction product. The present invention is predicated on these findings.

Brief Summary Text (18):

Examples of the polyfluoroalkyl group, which may contain at least one ether bond, are given below. ##STR8## Illustrative, non-limiting examples of the silane of formula (1) are given below. ##STR9##

Brief Summary Text (20):

In the practice of the invention, a partial hydrolyzate of the above-mentioned silane may also be used as component (A). At least one hydrolyzable group must be left in the hydrolyzate. If desired, a mixture of silanes or a partial hydrolyzate of mixed silanes may be used.

Brief Summary Text (22):

Illustrative, non-limiting examples of the silane of formula (2) are given below.

Brief Summary Text (32):

In the practice of the invention, a partial hydrolyzate of the above-mentioned silane may also be used as component (B).

Brief Summary Text (60):

In the practice of the invention, a partial hydrolyzate of the above-mentioned silane may also be used as component (C).

Brief Summary Text (63):

In the practice of the invention, a partial hydrolyzate of the above-mentioned silane may also be used as component (D).

Brief Summary Text (78):

Since the major component, fluorinated alkyl group-containing silane compound itself is given water solubility, the fiber treating agent of the invention is readily soluble in water and fully shelf stable. The fiber treating agent is not detrimental to the environment since it is aqueous. The water repellency thus imparted lasts long. Fibers treated with the agent undergo less yellowing. There is also described a method capable of producing the reaction product in a stable manner.

Detailed Description Text (39):

The treated fabric was dipped in a detergent liquid containing 5 grams of sodium alkylbenzenesulfonate and 2 grams of sodium carbonate in 1 liter of water. A household clothes washer was filled with warm water at 50.degree. C. together with the detergent liquid in a bath ratio of 1/100 and operated for 15 minutes. The washed fabric was subject to the spray type water repellency test.

Current US Cross Reference Classification (6):

8/115.64

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L8: Entry 27 of 51

File: USPT

Jul 12, 1994

DOCUMENT-IDENTIFIER: US 5328765 A

TITLE: Organic polymers having a modified surface and process therefor

Brief Summary Text (3):

It is well known in the art to surface treat organic polymers such as polyesters to improve the utility of such polymers. For example, it is known to treat polyester fibers to improve the adhesion of the polyester to substances such as rubber in the manufacture of tires. In U.S. Pat. No. 4,054,634, multifilament polyethylene terephthalate yarn is treated with a two-part finish, one part of which is applied after spinning and one part of which is applied after drawing. The first part contains a defined polyoxyethylated-polyoxypropylated monoether whereas the second part contains the monoether in combination with a defined epoxy ether silane and a sufficient amount of a water soluble alkaline catalyst to raise the pH to 8-10. Also see U.S. Pat. No. 4,348,517 wherein the same epoxy ether silane is combined with the triglycidyl ether of a glycerol and a defined diglycidyl ether and is used as a fiber finish for polyester yarn.

Brief Summary Text (4):

U.S. Pat. No. 3,793,425 also describes a process for improving the adhesion of Polyester material to rubber. In the process, undrawn polyester yarn is coated with a composition containing an epoxy resin which is preferably buffered with an alkaline agent, such as sodium carbonate, lithium carbonate, potassium carbonate or ammonium hydroxide. The use of epoxy resins with alkaline catalysts to improve the adhesion of polyester to rubber is further disclosed in U.S. Pat. Nos. 3,423,230 and 3,464,878.

Brief Summary Text (19):

The coreactant can be any cationic compound of an acid having a pK<sub>sub</sub>.a >2.5, preferably a pK<sub>sub</sub>.a >3.5. Suitable coreactants include alkali metal, quaternary ammonium, quaternary phosphonium, and alkaline earth metal hydroxides, bicarbonates, carbonates, sulfites, oxides and carboxylates like acetates, formates, propionates, caprates, octanoates, pelargonates, laurates, stearates, isostearates, oleates, dimerates; also alkoxides, aryloxides, borohydrides, dimethylsulfoxide salts, acetamide salts, hydrocarbon salts, and hydrides. Preferred cationic compounds for improved adhesion are those selected from the group consisting of quaternary ammonium and alkali metal hydroxides, bicarbonates, carbonates, and carboxylates like acetates, stearates, isostearates, laurates, octanoate, and dimerates. These compounds can, optionally, be buffered to an acidic pH below 7 with a volatile acid such as carbonic, acetic or propionic.

Detailed Description Text (4):

h e b b g e e e f c e

In this Example a blend was prepared containing 13.0 weight percent of a glycerol ether containing nominally four oxychloropropylene units with terminal 1-glycerol ether units, 1.6 weight percent potassium carbonate and 85.4 weight percent of a mixture comprising organomodified silicone, ethoxylated sorbitan mono-oleate, and ethoxylated octylphenol. Analysis of the glycerol ether showed it to have a hydroxyl value of 501 mgKOH/g, an organic chlorine content of 18.5%, an epoxy value of 0.03% (as epichlorohydrin) and a chlorohydrin value which was not detectable. The blend comprising 15 weight percent of an aqueous emulsion was applied as a spin finish using kiss rolls as the filaments exited the solidification zone and prior to drawing. The dry weight concentration of finish measured on the yarn after wind-up as determined by extraction with methanol was 0.59% which is representative of a reaction product concentration of 0.086 weight percent.

Detailed Description Text (10):

For purposes of comparison, a yarn produced as described above with the exception that a standard non-adhesive activating finish at a concentration level of 0.6% was applied in place of the finish containing the glycerol ether and potassium carbonate. The yarn was tested for adhesion and results (Control) are shown in Table 1.

Detailed Description Text (13):

The halohydroxy compound was used with potassium carbonate as a coreactant in a spin finish comprising on a dry weight basis: 13% halohydroxy compound, 1.6% potassium carbonate, and 85.4% of the same lubricating, emulsifying blend as employed in Example 1. This was applied to the yarn after solidification and prior to drawing from a 15% aqueous emulsion. The measured dry level of finish on yarn after wind-up was 0.53% weight percent which is representative of a reaction product concentration of 0.077 weight percent.

Detailed Description Text (17):

This halohydroxy compound was used with potassium carbonate as the coreactant in a spin finish, comprising on a dry weight basis: 17.5% halohydroxy compound, 2.0% potassium carbonate, and 80.5% of the same lubricating, emulsifying blend as used in Example 1. This finish was applied to the yarn after solidification but prior to drawing from a 15% solids aqueous emulsion. The measured dry level of finish on yarn after windup was 0.47% weight percent which represents a reaction product concentration of 0.092 weight percent.

Detailed Description Text (22):

The lubricating/emulsifying part of the composition applied as a spin finish comprised a pentaerythritol tetrapelargonate, a sorbitol ester ethoxylate, a castor oil ethoxylate, a decaglycerol hexaoleate and an antioxidant. The dry proportions of ingredients in the finish were: 15% halohydroxy compound, 0.97% potassium carbonate and 84.03% of the above blend of emulsifiers and lubricants.

Detailed Description Text (37):

The halohydroxy compound and the lubricants/emulsifiers were made into an aqueous emulsion and the rubidium carbonate was mixed with the emulsion. Carbon dioxide was added to reduce the pH to 7.8. The final emulsion comprising 15.0 weight percent solids was metered on to the yarn prior to drawing. After drawing, the concentration of the finish

on the yarn was 0.58 weight percent as measured by methanol extraction which represents a reaction product concentration of 0.096 weight percent.

Detailed Description Text (69):

Example 13 was repeated with the exception that after tensioning in the first stage, the cord was passed through an aqueous solution containing one part of the halohydroxy compound of Example 2, 0.8 part potassium bicarbonate and 100 parts water. The excess solution was blown off to achieve an application level of 0.2 dry weight percent on cord.

Detailed Description Text (72):

Example 14 was repeated with the exception that the aqueous adhesive solution consisted of one part of the halohydroxy compound of Example 1, 0.8 part of potassium bicarbonate, 75 parts water and 50 parts acetone for purposes of solubilizing the mixture. Adhesion data is shown in Table II.

Detailed Description Text (74):

Example 14 was repeated with the exception that potassium bicarbonate was omitted from the aqueous solution. The adhesion results are shown in Table II demonstrating the necessity of utilizing a coreactant to achieve the improved adhesion when compared with the results obtained in Example 14.

Detailed Description Text (81):

Example 14 was repeated with the exception that the aqueous solution consisted of 1.2 parts of the halohydroxy compound of Example 2 and 0.8 part of potassium bicarbonate (Example 19), or 0.55 parts of potassium carbonate (Example 20), and the heat treatment in stage 1 was adjusted to 350.degree. F. for 30 seconds dwell. Additionally, the pH of the aqueous solution of Example 20 is reduced by the addition of acetic acid to 7.0 (Example 21) and to 5.0 (Example 22). A control was prepared without the addition of the aqueous solution. The strength of treated cord increased as the pH was reduced.

Detailed Description Text (88):

Example 23 was repeated with the exception that after tensioning in the first stage, the carbon cord was passed through an aqueous solution containing one part of the halohydroxy compound of Example 2, 0.8 part potassium bicarbonate and 100 parts water. The excess solution was blown off to achieve an application level of 0.2 weight percent on cord.

Detailed Description Text (95):

Example 25 was repeated with the exception that after tensioning in the first stage, the Kevlar cord was passed through a solution consisting of 100 parts water, 50 parts acetone, 1.2 parts of an ether of glycerol with nominally 6 oxychloropropylene units, with terminal 1-glycerol ethers, and 0.80 part potassium bicarbonate before the heat treatment. The halohydroxy compound had a hydroxyl value of 347 mgKOH/g, an organic chlorine content of 23.5%, an epoxy value of 0.17% and a chlorohydrin value of 0.49%.

Detailed Description Text (101):

Example 27 was repeated with the exception that after tensioning in the first stage, polyethylene terephthalate cord was passed through an

aqueous solution consisting of 100 parts water, 2.4 parts of an ethanol ether nominally having two oxychloropropylene units and a terminal 1-glycerol ether, 0.55 part potassium carbonate and 0.20 part of aerosol OT (75 weight % solid) which is a sulfosuccinate wetting agent. The halohydroxy compound had a hydroxyl value of 282 mgKOH/g, an organic chlorine content of 23.8%, an epoxy value of 0.20% and a chlorohydrin value of 0.4%.

Detailed Description Text (104):

Example 13 was repeated with the exception that after tensioning in the first stage, the cord was passed through a solution in zone 1 containing 1.2 parts of a glycerol ether and 0.8 part of potassium bicarbonate in 20 parts of water and 80 parts of methanol. The glycerol ether was prepared by the combination of two etherified glycerol molecules wherein one 2,3 dihydroxypropyl end group from one molecule reacts with the epoxide of another molecule during the hydrolysis reaction to join the molecules through an ether linkage, and the resulting dimer contains on average approximately two and one-half 2-bromomethoxyethylene units and approximately one 2-hydroxymethoxyethylene unit together with uncombined 2,3-dihydroxypropyl end groups. The bromohydroxy compound had a hydroxyl value of 452 mgKOH/g, an organic bromine content of 23.1%, a low epoxy value of 0.02% and a bromohydrin content of 1.7%, and a weight average molecular weight of 834, as measured by gel permeation chromatography.

Detailed Description Text (107):

Example 14 was repeated with the exception that the aqueous solution contained 0.55 part triglycerol (trimerized glycerol commercially produced by Mazer Chemical Company), 0.55 part of a glycerol ether with nominally 1 oxychloropropylene group and terminal 1,3 glycerol ethers in which the 3-substituent is a 2-hydroxy propyl ether, 0.8 part potassium bicarbonate and 100 parts water. The halohydroxy compound had a hydroxyl value of 557 mg KOH/g, an organic chlorine content of 7.1% and an epoxy value of less than 0.1%.

Detailed Description Text (110):

Example 13 was repeated with the exception that after tensioning in the first stage the cord was passed through an aqueous suspension consisting of 100 parts water, 2.9 parts phenol blocked methylene bisphenylisocynate, 1.2 parts of the halohydroxy compound of Example 2, 0.80 part of potassium bicarbonate and 0.1 part sodium sulfo succinate wetting agent. The excess solution was blown off to achieve an application level of 0.8 dry weight percent on cord. The first stage temperature was set at 450.degree. F. for 50 seconds and the second stage was set at 420.degree. F. for 50 seconds. The RFL formulation employed in the second stage was that of Example 23.

Detailed Description Text (114):

The procedure of Example 14 was repeated except that 0.63 parts of calcium acetate was used rather than the potassium bicarbonate. The adhesion result of the steam aged specimen was 25-lbs. force and 2.2 rating vs. 6 lbs. force and 1.0 rating in the control, demonstrating that alkaline earth salts can be effective coreactants.

Detailed Description Text (128):

Example 35 was repeated with the exception that 0.55 part of potassium carbonate was added to the aqueous solution of the first stage. The

results of the adhesion testing are provided in Table X.

Detailed Description Paragraph Table (3):

Halohydroxy compound of Example  
1 20.00% Rubidium carbonate 3.84% Lubricants/emulsifiers of Example 1  
76.16%

Detailed Description Paragraph Table (4):

Halohydroxy compound of Example  
1 13.00% Rubidium carbonate 3.01% Carbon dioxide 0.57%  
Lubricants/emulsifiers of Example 1 83.42%

Detailed Description Paragraph Table (6):

Halohydroxy compound of Example  
4 15.00% Potassium bicarbonate 2.32% Lubricants/emulsifiers of Example  
1 82.68%

Detailed Description Paragraph Table (8):

Halohydroxy compound of Example  
4 15.00% Cesium carbonate 3.77% Lubricants/emulsifiers of Example 1  
81.23%

Detailed Description Paragraph Table (9):

Halohydroxy compound of Example  
4 15.00% Sodium carbonate 1.44% Lubricants/emulsifiers of Example 1  
83.56%

Current US Cross Reference Classification (3):  
8/115.54

CLAIMS:

7. The organic polymer of claim 4 wherein said cationic compound is selected from the group consisting of alkali metal and quaternary ammonium hydroxides, carbonates, bicarbonates, carboxylates and nitrites.

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L8: Entry 51 of 51

File: USOC

May 5, 1953

DOCUMENT-IDENTIFIER: US 2637623 A

TITLE: Textile treating compounds and method of applying them to  
textilesOCR Scanned Text (2):

2,637,6P,S 3 When Y is trivalent, the formula assumes this aspect: R3--Si-o-Y-N (tert) X (3) 5 R3-Si-O-Y-N (tert) X where A is an alkylene radical and the other radicals are as described above. A may also be an aromatic or cycloaliphatic radical. When Y is a bivalent hydrocarbon residue' 10 these compounds may be prepared from the cor- responding halogenosilane and epoxide, accord- ing to the procedure set forth in J. Am. Chem. Soc. 67 1548 (1945) 1. 15 (4-n)A + R@SiXt- - R.Si[OYXII-. RnSi[O-Y-N (tert) X]4-, @1 N (tert) 20 The general reaction, however, involves action of the corresponding alcohol, its chloromethyl ether, or quaternary ammonium salt on the halo- geno silane (Ann. Chim. Phys. (4) 9, 5 (1866); Ann. 488, 56 (19al) ; and J. Am. Chem. Soc. 68, 70 2 @) (1946): 4 These compounds are white or pale-colored solids, or viscous liquids, soluble or dispersible in water, pyridine, dioxane, xylene, mesityl oxide, benzene, chloroform, ethyl alcohol, carbon, tetrachloride, ethylene dichloride, ether and acetone. The quaternary ammonium group of these compounds is decomposed by heating the dry compound above about 90' C., liberating the tertiary amine and a radical of the form It may also be hydrolyzed by water at temperatures as low as 60 to 80' C., forming these products. in considering the possible reactions that may follow decomposition of this group, it must be borne in mind that the radical Y also influences the reactions which may occur. Y groups which include urea, amide or carbamate groups, and thus are of the form - CONHCH2- are readily polymerized; whether or not the silicon-oxygen linkage is hydrolyzed affect only the type of polymers formed. For example, if the compound contains two quaternary ammonium groups, linear polymers may form even though the silicon-oxygen linkage remain unhydrolyzed. Similarly, a hydroxy amide, urea, ester, carbamate or hydroxy hydrocarbon halide may be used, or their chloromethyl ethers or quaternary ammonium salts: The silicon-oxygen linkage is hydrolysable, but its ease of hydrolysis depends upon the number of carbon atoms of the R group attached to the silicon atom. Hydrolysis may be inhibited in the 3. 'HOC112CONIr2 - R.gi [OCH2@CONH2]4@. I HX + HCII@O + X(tett) R.SiX4- + HOCH2CON]12olr2N (tert)X-@ R.Si[OCH#CONH.CHIN(tert)'Xli- -N(tert)- HOClr2CONUClr2CI - R.sitocEric:ONHCHIO-i@-. 4. HOCHiNH.CGrNHi. R.Si[OCHiNHOONU 214-. I RX + IrCII0 + g(tett) R.Sixd- + HOCH2NHCO-NHCH2N(tert)X @ R.SI [OCH2NHCONUCEIN(tert)X" .N(tort) EEOCH2NHCONHCH2CI@ R.si[och2NE- ConNelriCI14-. HOCH2OOCCH2CI R.six4- + N(tort) OCH3OCC]Er2N(tort)CI R.S![O ClfiOOCCH2N(tert)Cl]" R'6-Si-[oc, H2cH2x]j.-. HOCH2CH2X R@Si-X3- + N(tert) I I R,-si-x3-. R.Si-i-O@CH2C]@f2N(tert)X],, HOCH2CMN(tert)X

h e b b g e e f c e

R.-S1--IOCH<sub>2</sub>CII2N(tert)Xls-. 2. EIO (C 1r2)20 H @ R.SI[O(CH<sub>2</sub>)20H]i-.  
IIIIX + ILC HO + N(tert) R.SIX4-. + HO(CH<sub>2</sub>)20CH<sub>2</sub>N(tert)X - R@Si[O(CH<sub>2</sub>)  
20CHIN(tert)X]4-. IN(tert) ,HO(CH<sub>2</sub>)20CH<sub>2</sub>CI @ R.SII0(CH<sub>2</sub>)20CH<sub>2</sub>CI14-.

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2,637,623. 9 it is desired to decompose the compound at the quaternary ammonium group only, or both it and the silicon-oxygen linkage. It is not necessary to hydrolyze the silicon-oxygen linkage. When it is stable to hydrolysis, 5 permanent water-repellency, softness and flame retardance in a 3t be impaired by merely decomposing the quaternary ammonium group in situ on the textile. In this event the impregnated textile is dried at a temperature low enough to inhibit decomposition of the quaternary ammonium group (see later) and then cured. This procedure gives good results with compounds such as octadecyldimethyl(ethoxyypyridinium chloride) silane and trimethyl (octadecyloxyypyridinium 15 chloride) silane. When it is desired to hydrolyze the silicon-oxygen linkage as well, it is possible by suitable steps first to bring about decomposition of the quaternary ammonium iodide group, and then to 20 hydrolyze the silicon-oxygen linkage. In this procedure, the impregnated textile is dried, cured at a temperature between about 80 and about 200° C., impregnated with a solution adapted to hydrolyze the silicon-oxygen linkage, and then 25 warmed at 40 to 150° C. and cured a second time at temperatures from about 30 to about 250° C. This procedure gives consistently good results with most of the compounds of the invention. It does require two impregnation, drying and two 3( baking steps, however.

Alternatively, both decompositions may be caused to occur simultaneously, or hydrolysis of the silicon-oxygen linkage may be made to occur first. 35 These procedures are quicker and more economical, since in the latter case the hydrolysis of the silicon-oxygen linkage may be made to occur in the first textile treating bath or directly thereafter, and the subsequent chemical reactions carried nearly to completion before the textile is dried, and then completed during the baking step, at which time decomposition of the quaternary ammonium salt also occurs, while in the former case both decompositions are made to 4,- occur during the first curing step. These procedures have the advantage of requiring only one impregnation, drying and curing. If the impregnated textile material is heated at temperatures above about 100° C. while still 50 wet, premature decomposition of the quaternary ammonium group may occur. 0 It is usually important that this be prevented, since in many instances no permanent effect may thereafter be obtained. In such cases, it is best to first dry the fabric thoroughly so that baking and curing may be carried out in the absence of moisture. Thick or tightly woven fabric especially must be dried with care, for they tend to retain moisture for a long period of time, even at elevated temperatures. The drying temperature is preferably between 30 and 80° C., but the temperature of drying is less important than the speed and other conditions. If the fabric is dried in more or less stagnant air, as in an oven 65 without artificial circulation, it should not be submitted to a drying temperature of more than 30° C. When, on the other hand, it is dried in a blast of hot air so that the water may be removed rapidly, say in about 3 minutes, then the drying: 70 temperature may rise to 80° C. Again, when the treated material is dried on a steam-heated cylinder at 120° C., no permanent effect may be obtained. The curing or baking temperatures should be 75 to 10 between 80° and 260° C. For decomposition of the quaternary ammonium salt,

temperatures between 80' and 150' C. are preferred, while curing of the silicone-containing reaction products may require temperatures up to 50' C. to 100' C. higher; that is, the preferred range in this case lies between 100 and 250' C. The time of baking is inversely proportional to the temperature used, and both depend to some extent on the nature of the compound and of the textile material. A longer baking time and a relatively low temperature should be used with thick or tightly woven fabrics in order that the heating may be uniform throughout, while open weave fabrics or fabrics of synthetic fibers, such as nylon, may safely be heated at higher temperatures. If tendering of the material is to be avoided, the time of baking is preferably kept as short as possible and the baking temperature as low as possible. In the case of open weave fabrics, if a brisk circulation of air is provided around and through the material, the preliminary drying step may be omitted and the treated material heated at once at the baking or curing temperature. The drying operation may be carried out in a covered tenter frame, while curing or baking is best carried out on a loom, mat, roll or air lay dryer. Hydrolysis of the silicon-oxygen linkage, which is usually accompanied by polyinierization and other chemical interaction of the hydrolysis products if  $n=2$  or 1, may be carried out in aqueous neutral, alkaline or acidic media at room or elevated temperatures. It may therefore occur spontaneously in the, initial treating solution. Addition of a substantial amount of a tertiary amine, from 0.5 to 1.5 moles of the amine per mole of the compound, seems to inhibit either the hydrolysis or the subsequent chemical reactions; upon volatilization of the amine in a later heating step, both reactions proceed as though it had never been present. It may also be carried out after impregnation and/or curing while the textile is traveling through a bath of the hydrolysing media, or while the textile is wet with such a medium or its vapors. Hydrolysis in neutral or alkaline solution favors formation of linear or cage type polymers, while hydrolysis in acidic media favors formation of cyclic silicon compounds. Acid hydrolysis may also be objectionable with cellulosic fabrics because tendering may result. It is desirable that only the stoichiometric amount of water to form the expected polymer be present, but this is not essential, and in fact is a condition almost impossible to attain after the compound has been applied to the textile. Hydrolysis may be carried out at from, 100 to 100' C., depending upon the ease of hydrolysis, as set forth previously. The reaction may be exothermic. Usually it is complete in 15 minutes to an hour, but it may require up to five hours. Solution pH values between about 5 and about 10 are preferred, but stronger solutions may be used where no fabric damage is caused. Bases such as sodium and ammonium hydroxide and acids such as hydrochloric or sulfuric are suitable. The chemical reactions subsequent to hydrolysis are expedited by higher temperatures, and should also be conducted in the presence of moisture, and/or an acid or base. Following hydrolysis, and without rinsing, therefore, the treated textile may be warmed while keeping it

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wet, as in a moist atmospl. Tere, from 10' to 150' C., for from 15 minutes to several hours, and then cured at 80' to 250' C. for a period, of a few minutes to several hours. Again, possible damage to the fabric governs the time employed. The cured fabrics may be washed and/or rinsed, prior to or after final curing, to remove acid or base, by products and unreacted material. Example 10 Dry ethylene oxide gas is bubbled slowly through one mole of

trimethylchlorosilane contained in a three-neck flask fitted with calcium chloride tube, a water-cooled reflux condenser and a gas inlet tube. Pressure inside the vessel is maintained at 15 psi above atmospheric and the chlorosilane is heated to boiling at the start of the reaction. The reaction is exothermic, so that no heating is required after reaction has begun. The reaction is permitted to continue for about two to three hours. The 2,2-dichloroethoxytrimethylsilane is recovered and purified by fractional distillation. The procedure is repeated using trichloromethylsilane, and the trichloroethoxymethylsilane likewise is recovered and purified by fractional distillation. Pyridinium hydrochloride is prepared by bubbling dry hydrogen chloride gas into a solution of 30% pyridine in d-Ky benzene. The pyridinium salt of each of the ethoxy silanes is prepared by pouring, the silane slowly, with constant stirring, into the pyridinium hydrochloride solution and then warming it at 40° to 80° C. until the quaternary formation of the corresponding pyridinium chloride of the formula:  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{N}^+ \text{Cl}^-$ . The compound is dissolved in a mixture of equal parts of pyridine and anhydrous ethanol to form an eight percent solution. A viscose rayon fabric is padded with this solution to a hundred percent pick up by weight. The fabric is then passed through a bath containing 1% sodium hydroxide solution and held at a temperature of 50° C., at a rate such that each section of the cloth remains in the solution for one-half hour. The wet cloth is warmed at 60° C. for another hour in a moist atmosphere to prevent evaporation. The fabric is dried at 60° C., baked at 150° C. for 15 minutes, and rinsed. The resulting fabric is flame resistant and shows improved water repellency, both of which are permanent to washing. Example 3: 200 parts of ethylene chloride and 220 parts of dry pyridine are heated together for 24 hours at 100° C., care being taken to exclude carbon dioxide. One mole of dimethyl dichloromethylsilane is placed in a 3-liter, three-necked flask fitted with a dropping funnel, calcium chloride tube and reflux condenser. To this is added, with cooling and over a period of two and one-half hours, the hydroxyethyl pyridinium salt precipitates. The precipitated hydroxyethyl pyridinium chloride solution is warmed at 60° until evolution of hydrogen chloride is stopped. The solution is filtered off and dried in vacuo. The salts have the formula:  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{N}^+ \text{Cl}^-$ . Equal parts of each salt, together with an equal weight of pyridine, are dissolved in water to form a ten percent solution. The pH of the solution is adjusted to 8.0 by addition of a small amount of triethanolamine. A cotton twill fabric is padded with the solution at room temperature to a 100% pick-up by weight. The treated fabric is warmed at 60° C. until dry and baked at 120° C. for three minutes. The fabric is then padded with a 0.3% solution of sodium hydroxide. Soaked at 40° C. During passage, the temperature of the wet cloth rises spontaneously to 60° C. Next, the fabric is removed from the padded and allowed to stand at room temperature in a moist atmosphere for two hours. It is then dried at 55° C. and cured by heating at 150° C. for 15 minutes. Finally, the fabric is washed with a soap solution, rinsed and dried. The material is water repellent, and also has good crease-resistance, dimensional stability and shrinkage resistance. Example 2: One mole of di-(1,3,5-trichlorophenyl)dichloromethylsilane is heated to 60° C. in a three-neck, round bottom flask fitted with calcium chloride tube, 0.5 reflux condenser and gas inlet. Ethylene oxide gas, is bubbled through the mixture until reaction is complete, which requires about three to six hours. The

mixture is distilled and the di-(2chloroethoxy) di(1,3,5-trichloroijhenyl) gilanere- 70 covered. one n-ole of the silane is dissolved in 350 cc. of dry benzene together with one mole of pyridine. Dry hydrogen chloride gas is bubbled through this solution while warming it at 50° C. until forina- j- 5 dtogen chloride ceases, and then subjected to a VACU-LIM to remove hydrogen chloride and excess pyridine, together with unreacted silane, and the pyridinium salt is recovered. This salt has the formula:  $(CH_3)_2Si-OCH_2CH_2NCl$  This procedure is repeated using trimethylchlorosilane. One part of trimethyl tetraethoxy pyridinium chloride) silane and two parts of dimethyl (diethoxy Pyridinium chloride) silane are dissolved in a solution containing equal parts of pyridine and water, to form a five per cent solution. This solution is padded on a wool fabric to a 100% pick-up by weight. The fabric is dried at 50° C. and then baked at 130° C. for 5 minutes. The cured fabric is immersed in a 0.5% sodium hydroxide solution and rinsed slowly through the solution so that each portion of the fabric remains in the solution for one hour. The temperature of the bath is held at 40, to 50, C. during the treatment. The fabric is then removed from the bath and allowed to regain in a humid oven at a temperature of 60° C. for two hours. The fabric is dried and cured at 175, C. for twenty minutes. The treated fabric, has improved dimensional stability and is water repellent. A nylon fabric treated in the same way and baked at 205° C. for five minutes in the initial step likewise has increased water repellency.

Example 4 Propylene oxide is bubbled into a mixture of

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13 methyl trichlorosilane and diethyl dichlorosilane held at 60° C., according to the procedure set forth in Example 1, until reaction is complete. The solution is then distilled to recover the mixture of propoxy silanes. The silanes are then added to a solution of pyridinium hydrochloride in benzene and the mixture warmed at 50° C. for one hour to form the corresponding pyridinium chlorides of the formulae:  $CH_3-Si-O(CH_2)_2-N-Cl$  13  $(CH_3)_2Si-O-(CH_2)_3-N-Cl$  12 These are dissolved in a mixture of equal weights of water and pyridine to form a ten per cent solution. An acetate rayon gabardine fabric is padded with the solution to 100% pick-up weight. The treated fabric is dried at 70° C. and then cured at 140° C. for 5 minutes. The cured fabric is immersed in a bath containing 1.5% aqueous sodium hydroxide, warmed at 50° C., for one hour. It is then warmed in a humid atmosphere in an oven at 60° C. for three additional hours and finally dried and cured at 160° C. for 20 minutes. The resulting fabric is water repellent, crease resistant and dimensionally stable. Example 5 One mole of  $\omega$ -chlorooctadecanol and 250 parts of pyridine are heated together for 24 hours at 100, C., care being taken to exclude moisture. The solution is added dropwise to two moles of trimethylchlorosilane contained in a three-necked, 2-liter flask fitted with reflux condenser, dropping funnel and calcium chloride tube. The flask is kept at 9, temperature of 500 C. during the reaction and addition of the pyridinium halide continued over a period of three hours. Reaction is continued until evolution of hydrogen chloride ceases. The mixture is then subjected to a vacuum to remove unreacted pyridine and trimethylchlorosilane. The quaternary pyridinium halide is recovered. This compound has the formula:  $(CH_3)_3Si-O-CisH_{36}-N-Cl$  This compound is dissolved in water to form an eight per cent solution whose pH is adjusted to 8 by addition of triethanolamine. A cotton poplin fabric is padded with this solution to 9, 100% pick-up by weight. The fabric is dried at 60° C. and then baked at 130, C. for

3 minutes. The cured fabric is immersed in a 5% sodium hydroxide solution which is warmed to 600 C. Passage through the solution is regulated so that the fabric remains therein for one-half hour. The fabric, while still wet, is then warmed at 80- C. for an additional 30 minutes in a moist atmosphere and then heated rapidly to 150' C. and held at that temperature for 10 minutes. The resulting product is water repellent and shows improved dimensional stability. 2,637,623 14

Example 6 One mole of octadecyldimethylchlorosilane is placed in a three-neck, two-liter flask fitted with reflux condenser, calcium chloride tube and gas inlet tube. The silane is heated to 50-60- C. and ethylene oxide then bubbled through the mixture until reaction is complete. This may be evidenced by failure of the mixture to gain additional weight. The mixture is then subjected to a vacuum to remove unreacted silane. The octadecyldimethylchloroethoxysilane may be purified by fractional distillation at 2 millimeters pressure. 15

Pyridinium hydrochloride is prepared by bubbling dry hydrogen chloride into a solution of pyridine in dry benzene. The chloroethoxysilane is added slowly to this solution while warming the latter to 60, and with rapid stirring. 20 The pyridinium halid, - which forms has the formula:  $\text{Cl}_3\text{N}(\text{CH}_3)_2\text{SiOCH}_2\text{CH}_2\text{N}-\text{Cl}$  This compound is dissolved in water to form a 10% solution. A rayon- fabric is padded with 30 this solution to a 100% pick-up by weight, dried at 70, C. for one hour and then baked at 140' C. for 5 minutes. After rinsing, a sample of the fabric shows good water repellency. The remainder of the cured fabric is immersed in a 35 bath containing an aqueous 1% solution of sodium hydroxide held at 651 C. and travelled through it at such a rate that a given portion remains in the bath for one-half hour. The fabric is then dried slowly at, 801 C. and finally 1, (' cured at 150- C. for 15 minutes, rinsed and dried. The treated fabric shows a somewhat better water repellency than the other sample, but both portions are satisfactory. 45 Example 7

One mole of dimethyldichlorosilane is placed in a three-necked two-liter flask fitted with stirrer reflux condenser, dropping funnel and calcium chloride tube. To this is added dropwise a solution of & - or X-hydroxystearamide dissolved in petroleum ether. The reaction mixture is kept at a temperature of 601 C. and heating continued until evolution of hydrogen chloride ceases. To 55 the solution is added one mole of laurylmaldehyde. The mixture is heated to 401 C. and dry hydrogen chloride bubbled through the solution until the chloromethyl compound is formed. Water from the reaction is removed as it is 60 formed by a trap affixed below the reflux condenser. Reaction is complete when no further water is liberated. The solvent and excess hydrogen chloride are removed by subjecting the solution to a vacuum and the chloromethyl compound 65 so obtained is added dropwise to an excess of pyridine at 40' C. The precipitate which forms is separated and dried in vacuo. The w- hydroxy derivative has the formula: 70  $(\text{Cl}_3\text{N})_2\text{Si}-\text{O}-\text{C}_17\text{H}_{34}-\text{CO}-\text{NH}-\text{CH}_2-\text{NCl}$  75

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2,637,623, is while the X-hydroxy derivative has the formula:  $(\text{Cl}_3\text{N})_2\text{Si}-\text{O}-\text{C}_17\text{H}_{34}-\text{CO}-\text{NH}-\text{CH}_2-\text{NCl}$  The compound is dissolved in water to form a 6,70 solution by weight. A cotton fabric is padded with this solution to 100% pick-up by weight, dried at 50, C. and then baked at 110' C. for onehalf hour. The cured fabric is immersed in a bath containing 1% ammonium hydroxide solution for one and one-half hours. During this 15 period the temperature of the bath rises to 35-401 C. The treated fabric is then warmed to 60' C. in a moist atmosphere, to prevent loss of water, for an additional hour, and is then dried, and cured at 125' C. for one

hour. The product 2t) obtained using either compound is Permanently water repellent and also shows a high degree of dimensional stabilization. Example 8 one mole of triethylchlorosilane is placed in a 1-5 three-necked round bottom flask fitted with mercury-sealed stirrer, calcium chloride tube and dropping funnel. The silane is warmed to 601 C. and to it is added, dropwise, with constant stirring, a solution of monomethylolurea in benzene. The mixture is heated at this temperature until evolution of hydrogen chloride ceases. The mercury-sealed stirrer is replaced with a water-cooled reflux condenser. To the reaction mixture is added one mole of paraformaldehyde dispersed in dioxane and dry hydrogen chloride is then bubbled through the mixture. Water which is liberated is separated as it is formed in a trap affixed below the reflux condenser. Reaction is continued by warming the mixture at 601 C. until evolution of water has ceased. Excess hydrogen chloride gas and solvent are removed by subjecting the mixture to a vacuum and warming at 401 C. The compound which separates is added in small amounts to an excess of pyridine -115 with rapid stirring, and the resulting mixture is warmed gently at 50' C. for a short period. The pyridinium chloride, of the formula 50 is recovered and dried in vacuo. 55 This procedure is repeated with dimethyldi- chlorosilane in place of triethylchlorosilane, and the analogous salt obtained. Both compounds, in the ratio of one part of the former to two parts of the latter, are then dissolved in a solution containing equal weights of water and pyridine to form a 10% solution by weight. Cotton, wool and rayon fabrics are individually padded with this solution at room temperature to a 100% pick-up by weight and dried at 60' C. The dry fabrics are heated at 1251 C. for ten minutes and divided into two portions. One portion is passed slowly through a bath heated to 501 C. and containing aqueous 2,110 sodium hydroxide solution. The travel time of 1-0 the cloths through the bath is one hour. The other portion of the cloths is passed through a bath heated to 40' C. containing 2% hydrogen chloride solution. All the cloths are held at 601 C. 16 baked at 1501 C. for 20 minutes, and rinsed. The products show a high degree of permanent water repellency, crease-resistance and dimensional stability. Example 9 Dimethyldi (oxylaurylcarbamylmethylene pyridinium chloride) silane, of the formula: (CEli), @'10-C12EE240 C ON-H C MN Cl is prepared using the procedure of Example 7, &)-hydroxylalyl carbamate being employed instead of co-hydroxystearamide. This compound is dissolved in water to form an 8% solution by weight. A rayon-cotton gabardine fabric is padded with this solution to a 100% pick-up, dried at 80' C., and then baked at 110' C. for 5 minutes. The cured fabric is padded with a 2% sodium hydroxide solution at 601 C., allowing it to remain in the bath for 20 minutes, and then warmed, while still wet, at 601 C. for two hours and cured at 1601 C. for 15 minutes. The resulting fabric is permanently water repellent. Example 10 To one mole of 1,10-decamethyleneglycol in a three-necked, two-liter, round bottom flask fitted with mercury-sealed stirrer, calcium chloride tube and dropping funnel, is added, dropwise, over a three-hour period, one mole of dimethyloctadecylchlorosilane. Reaction is continued at 60' C. until evolution of hydrogen chloride ceases. Excess hydrogen chloride is then removed in a vacuum, the reaction mixture is dissolved in benzene, and one mole of paraformaldehyde added. The stirrer is replaced with water reflux condenser and the dropping funnel with a gas inlet tube. Dry hydrogen chloride gas is bubbled through the mixture, which is heated to reflux, until the solution becomes clear. Water which forms in the course of the reaction is removed by

a tray affixed below the Teflon condenser. The mixture is then subjected to a vacuum to remove benzene and excess paraformaldehyde and hydrogen chloride. The product is added in small amounts to an excess of pyridine, and the mixture is warmed until the pyridinium chloride separates. This is filtered and dried in vacuo. This compound has the formula:  $C_1H_37(CH_3)_2Si-O-(CH_2)_2-O-CH_2$ . A sufficient quantity of the compound is dissolved in a mixture of equal weights of pyridine and water to form a 5% solution, which is then applied to a rayon fabric. The fabric is dried at 50°C. and cured at 110°C. It is then passed slowly through a bath held at 75°C. and containing an aqueous 2.5% sodium hydroxide solution, so that the travel time is one hour. The cloth is squeezed to a 1005% pickled, -up and then rinsed and finally baked in a humid atmosphere or with steam at 100°C. for one hour and at 150°C. for 15 minutes. The cured cloth is rinsed and dried. The product is permanently water repellent and dimensionally stable. Example 11 One mole of dioctadecylideworosilane is placed in a moist atmosphere for one hour, and then 75 in a three-necked flask fitted with mercury-

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17 sealed stirrer, calcium chloride tube and dropping funnel, and heated to 600°C. To this is added, dropwise, over a three-hour period, with constant stirring, one mole of hydroxymethyl α-chloro acetate. Heating is continued until evolution of hydrogen chloride ceases. The reaction product is subjected to a vacuum in order to remove hydrogen chloride gas, and is then added slowly, in small quantities, to an excess of pyridine heated to 40°C. The pyridine solution is then warmed to 60°C. until separation of pyridinium halide, which has the formula:  $(C_1H_37)_2Si-10-CH_200-C-CH_2N-Cl_2$ . This compound is applied to a cotton fabric using the procedure set forth in Example 10. The treated fabric shows excellent water repellency. Example 12 Two moles of hydroxy acetamide are added in small portions to 2 moles of trimethylchlorosilane, heated to 60°C. in a three-necked flask fitted with mercury-sealed stirrer, reflux condenser, calcium chloride tube and dropping funnel. Heating is continued until evolution of hydrogen chloride ceases. The product is subjected to a vacuum to remove hydrogen chloride and unreacted chlorosilane. 1.5 moles of the silane is then heated with 0.75 mole of paraformaldehyde in a vacuum until evolution of water ceases. (See French Patent No. 782,330.) The product is recrystallized from carbon tetrachloride. One mole of the resulting diamidomethane and one mole of paraformaldehyde are mixed with 300 parts of benzene. The mixture is heated at 60°C. and stirred. Dry hydrogen chloride gas is passed in, until when a test portion is cooled no solid is seen to separate. The mixture is allowed to settle and the benzene solution is removed from the lower aqueous layer. Benzene and hydrogen chloride gas are removed under reduced pressure and the chloromethyl compound recovered. This is added in small amounts to an excess of pyridine. The pyridine is warmed at 60°C. until the pyridinium halide separates. This is filtered off and dried. It has the formula:  $(CH_3)_3-Si-O-OH_2-C_6O-N-CH_2-N-CH_2$ . This compound is dissolved in a solution containing equal weights of pyridine and water, to form an 8% solution by weight. This solution is applied to a rayon fabric using the procedure of Example 5. The resulting product is permanently water repellent. Example 13 1,1,3,3 - tetramethyl - 1,3,di - 2 - chloroethoxydisiloxane is prepared by adding 200 cc. of cold water to a cold mixture of 2 moles of dimethyl 1,2-chloroethoxychlorosilane and 1.3

moles of pyridine. The two layers which form are separated, and the upper layer washed several times with 15% sodium hydroxide solution and then dried over calcium chloride. Unreacted silane is removed by fractional distillation in vacuum. 2,637,623 is The disilicate is then added in small portions to an excess of pyridine and the resulting mixture warmed at 60° C. until separation of the pyridinium chloride, which has the formula:  $(CH_3)_2-Si-O-CH_2-CH_2-NH_3^+$   $\left<@: \right> 10 (CH_3)_2-di-O-CH_2C]_{12-N}$  10 ci This compound is dissolved in a solution containing equal weights of water and pyridine to form a 5% solution. A rayon fabric is padded with this solution to 100% pick-up by weight. It is then dried at 60° C. and cured at 130° C. for 3 minutes. The cured fabric is rinsed and then immersed in 1% aqueous sodium hydroxide solution for one hour at 60° C. It is then warmed in an oven at 60° C. in a humid atmosphere, dried 20 and cured at 150° C. for 15 minutes. The resulting product is water repellent and shows improved shrink resistance. Example 14 2.5 One part of trimethyl(ethoxy pyridinium chloride) silane and two parts of dimethyl di(ethoxy pyridinium chloride) silane are dissolved in water, to form an eight per cent solution. The pH of this solution is adjusted to 9 by addition of triethanolamine. This solution is padded at room temperature on a cotton-rayon fabric to a 100% pick-up by weight. The fabric is heated in an oven at 100° C. in steam of a humid atmosphere for one-half hour, dried and then baked at 150° C. for 15 minutes and rinsed. The treated fabric is dimensionally stable and water repellent. Example 15 Equal parts of methyltriethoxy pyridinium chloride silane and dimethyldiethoxy pyridinium chloride silane, together with an equal weight of pyridine, are dissolved in water to form a ten per cent solution. The pH of the solution is adjusted to 8.5 by addition of a small amount of triethanolamine. A rayon fabric is padded with the solution at room temperature to a 100% pickup by weight. The treated fabric is then warmed at 80° C. for one hour in a moist atmosphere, dried, and baked at 120° C. for one hour and at 160° C. for three minutes, rinsed and dried. It then exhibits good water repellency and crease resistance. Example 16 5.5 A mixture of methyl tri(propoxypyridinium chloride) silane and trimethyl propoxy pyridinium chloride silane, prepared according to the procedure set forth in Example 1, is dissolved in water in the presence of an equal weight of 60% pyridine to form a six per cent solution. A rayon fabric is padded with the solution to 100% pickup by weight. The treated fabric is warmed at 70° C. for one hour and then at 85° C. for one hour in a humid atmosphere, and then cured at 140° C. for 35 minutes. The cured fabric is rinsed and dried. It exhibits permanent water repellency, crease resistance, and dimensional stability. Example 17 70 Trimethyl(ethoxytributyl quaternary ammonium chloride) silane is dissolved in water to form an eight per cent solution whose pH is adjusted to 9 by addition of triethanolamine. A cotton fabric is padded with this solution to a 100% 75 pick-up by weight. The fabric is warmed in a

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2,687,623 19 humid atmosphere at 60° C. for one and one-half hours, dried, and then baked at 150° C. for 15 minutes, washed with soap solution and rinsed. The resulting product is permanently water repellent. 5 Example 18 Octadecyldimethyl(ethoxy pyridinium chloride) silane is dissolved in water to form a 10% solution. A rayon fabric is padded with this solution to a 100% pick-up by weight, dried at 70° C. and then baked at 140° C. for 5 minutes, washed with aqueous 10%

sodium bicarbonate solution, rinsed and dried. The cured fabric is then permanently water repellent. 15 Example 19 Trimethyl (oxystearamidomethyl pyridinium chloride) silane is dissolved in water to form an 8% solution by weight. Wool and cotton fabrics are padded with this solution to 100% 20 pick-up, dried at 50, C. and then baked at 110' C. for 15 minutes, washed with soap solution, rinsed and dried. The resulting products are permanently water repellent. The following is claimed: 25 1. Compounds having the general formula:  $R''-Si[-O-Y-iN(tert)X]4^-$ . where n is an integer from 1 to 3; R is selected from the group consisting of saturated alkyl hy- 30 drocarbon radicals, alicyclic hydrocarbon radi- cals and aryl hydrocarbon radicals having fr Om 1 to about 20 caxbon atoms; Y Is a bivalent bridg- Ing radical selected from the group consisting of alkylene arylene and cycloalkylene hydrocarbon 35 radicals having from 1 to about 30 carbon atoms; N(tert) is a tertiary amine selected from the group consisting of tertiary aliphatic amines and tertiary heterocyclic amines; and X is a chlorine atom. 40 2. Compounds having the formula  $R@Si[O(CH_2)@NC_5H_5Cl]4^-$ . where n is an integer from 1 to 3, R is an alkyl hydrocarbon radical having less than 20 carbon atoms, and y is an integer from 1 to 30. 45 3. Trimethyl(ethoxy pyridinium chloride) silane. 4. A process of treating organic textile materials to modify the physical characteristics thereof which comprises impregnating said material 50 with from about 0.1 per cent to 20 per cent by 20 weight of said material of a compound of claim 1 in aqueous solution, drying said material at a temperature of less than about 1001 C., and heating said material to a temperature of from 80' to 260' C. to decompose the quaternary ammonium compound while leaving the siloxy linkage intact and to bond the reaction products to the material. 5. A process of treating organic textile material to modify the physical characteristics thereof which comprises impregnatiig said material with from about 0.1 per cent to 20 per cent by weight of said material of a compound of claim 1 in aqueous solution, drying said material at a temperature of less than about 100 C., heating said material to a temperature of from 80, to 260' C. to decompose the quaternary ammonium compound, then hydrolyzing the siliconoxygen linkage of said compound, warming said material at a temperature of from about 40' to 150' C. and, finally, heating said material to a temperature of from 80' to 2501 C. to bond the reaction products to said material. 6. A process of treating organic textile material to modify the physical characteristics thereof which comprises impregnating said material with from about 0.1 per cent to 20 per cent by weight of said material of a compound of claim 1 in aqueous solution, hydrolyzing the silicon-oxygen linkage of said compound, warming said material at a temperature of from 40' to 80' C., drying said material at a temperature of less than 100' C. and, finally, heating said material at a temperature of froin 80' to 250, C. to bond the reaction products thereto. 7. The process as in claim 6 wherein the solution with which said material is impregnated has a pH of from about 5 to 10 whereby said- hydrolysis is efic'eeted concurrently with said impregnating step. JOHN ROBERT JANES. References Cited in the file of this patent UNITED STATES PATENTS Number Name Date 2,258,218 Rochow ----- Oct. 7, 1941 2,277,174 Krefeld ----- - Mar. 24, 1942 2,415,017 MacKenzie ----- Jan. 28, 1947 2,462,635 Haber ----- Feb. 22, 1949 OTHER REFERENCES Dearing et al.: Journal American Chemical Society, volume 50 (1928), pages 3058 to 3062..

Current US Original Reference Classification (1):

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8/115.64

Current US Cross Reference Classification (14):  
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L8: Entry 38 of 51

File: USPT

Jan 29, 1985

DOCUMENT-IDENTIFIER: US 4496363 A  
TITLE: Antimicrobial fabrics

Brief Summary Text (12):

Examples of aminoalkyl silanes which may be utilized in this invention include 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropyltripropoxysilane, 3-aminopropyltributoxysilane, 3-aminopropyltripentoxysilane, 3-aminopropyldimethoxyethoxysilane, 3-aminopropyldiethoxymethoxysilane, 3-aminopropylmethoxyethoxypropoxysilane, 3-aminopropyldimethoxymethylsilane, 3-aminopropyldimethoxyethylsilane, 3-aminopropylmethoxyethoxypropylsilane, 4-aminobutyltrimethoxysilane, 5-aminopentyltrimethoxysilane, 6-aminohexyltrimethoxysilane, 10-aminodecyltrimethoxysilane, N-(3'-aminopropyl)-3-aminopropyltrimethoxysilane, N-(3'-aminopropyl)-3-aminopropyltriethoxysilane, N-(2'-aminoethyl)-3-aminopropyltrimethoxysilane, N-(3'-aminopropyl)-4-aminobutyltrimethoxysilane, etc.

Brief Summary Text (13):

Typically, aminoalkylsilylation is performed by contacting the base fabric and aminoalkylsilane at ambient, or a slightly elevated, temperature for a time sufficient to ensure silylation. Although a temperature less than about 50.degree. C. will suffice, more elevated temperatures are not detrimental and will result in a shortened reaction time. When a shorter reaction time is desirable, a more elevated temperature is advantageous. Contact time will depend on temperature, and may range from minutes to about 18 hours. After reaction is complete, excess silane is removed by decantation, and adhering but unreacted material often is removed by washing the fabric.

Detailed Description Text (4):

Three or four pieces of similarly treated cloth were placed in a flask. To each such flask was added 100 ml of a 1 mg/ml solution in 0.1 M potassium phosphate buffer, pH 7.0, of either zinc bacitracin A, polymixin B, or egg white lysozyme which had been filter sterilized using a Nalgene type-S, 120-0020, 0.2 micron filter. The polymixin B sulfate had an activity of 7400 USP units/mg; lysozyme had 41,000 E.sub.282.sup.1% units/mg; bacitracin A had 59,400 units/g. Immobilization proceeded overnight at room temperature on an orbital shaker with agitation for 10 seconds every minute. After decantation of the antimicrobial solution, the swatches were washed with two 100 ml- portions of 2 M sodium chloride solution for a 5 minute period with agitation followed by an overnight wash in running sterile water.

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